doi:10.1017/S1431927614003985
Microsc. Microanal. 20 (Suppl 3), 2014

Probing Electrochemical Cycling Stability of Li-ion Cathode Materials at Atomic-scale

Miaofang Chi,[1] Bo Xu,[2] Christopher R. Fell,[2] Shirley Meng,[2] and Jihui Yang[3]

[1] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[2] Department of NanoEngineering, University of California - San Diego, La Jolla, CA 92093
[3] Department of Materials Science & Engineering, University of Washington, Seattle, WA 98195

Li-excess layered oxide high energy density materials are currently being considered as promising candidates for energy storage technologies in plug-in hybrid electric vehicles (PHEVs) or electric vehicles (EVs), owning to their high capacity (>250mAh/g), high energy density, and excellent safety.[1-3] Two major fundamental questions, however, must be resolved before their commercial implementation: one is the irreversible capacity loss during the first electrochemical charge and the other is the voltage decay after long-time cycling.[4] Much of the recent research focus has been devoted to addressing these two issues. Possible explanations for the observed performance loss have been proposed: the irreversible loss of oxygen from the structural lattice and surface phase transformations upon electrode/electrolyte reduction.[3,5] The underlying mechanisms controlling performance, however, are unclear due to a present lack of understanding of the material's nm-scale characteristics.

As these materials undergo significant elemental migration and reduction/oxidation upon electrochemical charge-discharge cycling, the local structural and compositional evolution of the lattice upon cycling, both in the bulk and on the grain/particle surfaces, are the key parameters controlling capacity behavior. Advanced analytical electron microscopy (AEM), combining Z-contrast imaging, annular bright field (ABF) imaging, and electron energy-loss spectroscopy (EELS), offers an ideal platform for probing the local crystalline, chemical, and electronic structures simultaneously at the atomic-scale. In this study, Li-excess $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ (LMNO) subjected to different charge states within the first cycle and with different cycling times, were analyzed and compared by AEM. Co-doped LMNO samples were also investigated to evaluate doping effects on capacity and voltage degradation.

LMNO specimens at different charge states and after different cycling times were analyzed and compared. AEM results show that the atomic structure and chemistry of the bulk regions of individual LMNO grains are preserved, even after 80X cycling. The ordering occupancies of the transition metals (TM) and Li in the TM layers were clearly resolved in the pristine sample, and such structures were still observed in the specimen after 10X cycling (Figure 1a). However, atomic re-arrangement occurred at the grain surfaces to a depth of 4-5 unit cells, even after the initial cycle. In these surface regions, both of the Li-sites, i.e., those on the Li- and TM-layers, were occupied by greater numbers of TM atoms, forming a spinel-like structure, as opposed to the starting perovskite layered structure. Its formation partially blocks the Li transport pathways into the LMNO particles. First principle calculations further supported the formation of such spinel-like surface structures (Figure 1b).[4] This atomic rearrangement continues to increase in thickness with increasing cycling times. After 18X cycles, a nano-crystalline spinel surface layer was formed on the particle surfaces, acting as a protective layer/coating, preventing further surface phase transformation of the LMNO, but also inhibiting Li transport. Analysis of LMNO samples after much longer cycling times (60X) support this assumption.

In addition to the direct observation of the microstructural evolution at the particle surfaces, the chemical composition and electronic structures were studied for the LMNO grain interiors and surfaces after charging for different cycling times. Cycled materials showed clear Li-deficiencies on the particle surfaces corresponding with the layered-to-spinel surface structure transformation. Li loss on the surfaces of 10X-cycled grains is ~40% according to EELS quantification (Figure 2). [4] A decrease in the valence state of Mn was observed on the cycled particle surfaces, from Mn^{3+} to Mn^{2+}, which is consistent with the structural transformation identified. No significant oxygen vacancies were observed for samples at different cycling stages, in contrast with results from previous studies. [6] The present results indicate that oxygen vacancies might not be the primary source of voltage decay in LMNO. Instead, the migration of Mn ions likely plays an important role in terms of both large capacity loss in the first cycle and voltage decay with long cycling times. The results pave the way to a fundamental understanding of the degradation mechanism of oxide cathode materials in Li-ion batteries.[7]

References:

[1] Lu, Z., MacNeil, D. D., Dahn, J. R., Electrochem. Solid State Lett., 2001. 4(11): p. A191.
[2] Grey, C. P., Yoon, W. S., Reed, J., Ceder, G., Electrochem. Solid State Lett., 2004. 7(9): p. A290.
[3] Thackeray, M. M., Kang, S. H., et. al. J. of Mater. Chem., 2007. 17(30): p. 3112.
[4] Xu, B., D. N. Qian, et al. (2012). Mater. Sci. & Eng. R., 73(5-6): p51.
[5] M. Jiang, B. Key, Y.S. Meng, and C.P. Grey, Chem. of Mater., 2009. 21(13): p. 2733.
[6] Lu, Z. H. and J. R.. Dahn, J. Electrochem. Soc. 149 (2002) A815.
[7] Microscopy supported by ORNL's Center of Nanophase Materials Sciences, which is sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy.

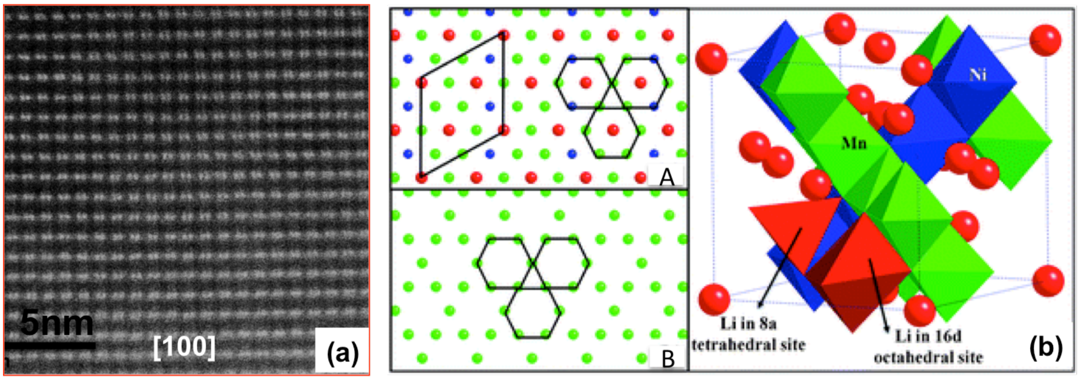

Figure 1. (a) Z-contrast STEM reveals the atomic structural stability of bulk LMNO after 10X cycles; (b) defect-spinel model of $Li[Ni_{1/4}Li_{1/6}Mn_{7/12}]O_2$ and $Li[Li_{1/3}Ni_{1/2}Mn_{7/6}]O_4$ (b).[4]

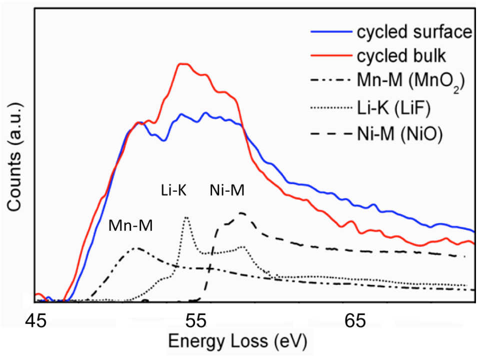

Figure 2 EELS quantification of Li concentrations on the grain surface and grain interior (bulk) of the LMNCO sample after 10X cycles.